



RESEARCH ARTICLE

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Classification of Hungarian medieval silver coins using x-ray fluorescent spectroscopy and multivariate data analysis

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Abstract

Background: A set of silver coins from the collection of Déri Museum Debrecen (Hungary) was examined by X-ray fluorescent elemental analysis with the aim to assign the coins to different groups with the best possible precision based on the acquired chemical information and to build models, which arrange the coins according to their historical periods.

Results: Principal component analysis, linear discriminant analysis, partial least squares discriminant analysis, classification and regression trees and multivariate curve resolution with alternating least squares were applied to reveal dominant pattern in the data and classify the coins into several groups. We also identified those chemical components, which are present in small percentages, but are useful for the classification of the coins. With the coins divided into two groups according to adequate historical periods, we have obtained a correct classification (76-78%) based on the chemical compositions.

Conclusions: X-ray fluorescent elemental analysis together with multivariate data analysis methods is suitable to group medieval coins according to historical periods.

Keywords: X-ray fluorescence spectroscopy, Multivariate techniques, Coin, Silver, Middle ages

Introduction

Elemental analysis is used for the examination of coins and other metal objects in the field of archeology. By determining the elemental composition of an object, one can find out about the used ore and its origin, as well as the age of the artifact. One can also come to conclusions about economic history, based on the changes of concentrations of various elements over time in the coins. In the medieval ages, minting workshops were usually built close to mines, so the identification of the precious metal mines could also mean the determination of the place of coinage.

The aim of research was to assign the coins to different groups with the best possible precision based on the acquired chemical information and to build models, which arrange the coins according to their historical periods.

Discovering relationship between elemental composition of coins and their origin has begun in the past 10-15 years with energy dispersive X-ray fluorescence spectroscopy devices (XRF). Publications, which connect elemental compositions to historical periods can be found scarcely in the literature, moreover only principal component analysis is applied for the evaluation of the data.

Greek and Romanian researchers used X-ray fluorescence spectra to categorize antique coins made between the 4th and 1st centuries B.C., by their places of origin and recovery [1,2].

In another paper two types of medieval coins were examined with XRF, proton-induced X-ray emission analysis (PIXE) and scanning electron microscopy (SEM/EDX) [3]. Data were evaluated with principal component analysis and the aim was to classify the coins by their places of origin [3]. It was concluded, that PIXE was less appropriate for the measurement of corroded coins due to its lower depth of penetration. The classification of coins into two groups was successful and so was the recognition of unknown samples.

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Similar measurements were carried out on coins from the eras of the Spanish War of Independence and of Ancient Greece [4,5]. They were partially successful in classifying the coins according to their places and time of coinage [4,5].

Besides the determination of places of origin, X-ray spectra and elemental compositions can also be applied to rule out counterfeit coins. Minemasa Hida et al compared counterfeit and valid 500¥ coins by elemental composition [6]. The coins were successfully differentiated by PCA, as well as by cluster analysis. Moreover, two separate clusters were identified within the group of counterfeit coins [6].

Another interesting application of manual XRF devices is to determine limits of detection through various kinds of packaging: potentially they could be used to rule out post bombs and other explosives [7]. As we can see, measurements carried out with XRF are useful in supporting not only the work of archaeologists, but also the work of the authorities.

Methods

X-ray fluorescence spectroscopy

During X-ray fluorescent analysis [8,9] the surface of a sample is irradiated by X-ray beam. By applying the appropriate energy, a photoelectron is emitted. The vacancy then is filled by an outer electron, while the energy difference is emitted in the form of X-ray fluorescent radiation. The excitation energies correspond to the emission lines of the elements, while the intensity of the emission provides information about their concentration on the sample surface.

The X-ray fluorescent technique provides quick non-destructive analysis. It gives information about the composition of metallic and non-metallic surfaces without the need for any pretreatment. The technique is independent from the chemical state of the elements, but it doesn't give information about the chemical bonds (oxidation state) of the examined elements. During a measurement with an appropriate excitation source, all of the elements in the sample can be examined simultaneously. This method enables the study of both solid and liquid substances.

We applied an INNOV-X Alpha handheld analyzer for our studies, which can easily measure concentration of elements heavier than sodium with 0.01% precision from very different matrices. According to recent research, handheld devices can produce equally accurate results as benchtop XRF analyzers in the study of coins [10].

Instrument specifications

- Excitation source: X-ray tube, W anode, 10-40 kV, 10-50 μ A.
- Detector: Si PiN diode detector, <230 eV FWHM at 5.95 keV Mn K-alpha line.

- Standard elements: Pb, Cr, Hg, Cd, Sb, Ti, Mn, Fe, Ni, Cu, Zn, Sn, Ag, As, Se, Ba, Co, Zr, Rb.

Principal component analysis (PCA)

Principal component analysis [11-14] is known by several names in different areas of science, so it can also be found in articles as "eigenvector analysis" or "characteristic vector analysis". PCA is unsupervised, so we don't classify the samples before the analysis. The basic idea is that we place our measured data in a data matrix (marked X), in which the rows correspond to the samples (in this case, coins), whilst the columns represent the studied properties (here: metal concentrations). This matrix can be decomposed into the product of two matrices. There are an infinite number of resolutions, but with constraints like orthogonality and normalization the solution becomes definite (aside from central mirroring). During standardization we first shift our original scale by a constant number and then shrink or expand it, so that the arithmetic mean of the property vectors becomes 0 and their deviation 1. The resulting matrices are the score (T) and factor loading (P) matrices.

PCA can be applied to rule out outliers, to reduce our dataset (which can ease our work greatly in cases of big, complex datasets) and to build models that describe the behavior of a physical or chemical system and reveal any pattern in the data. The models can be used for predictions when we introduce new data (new samples measured in the same way).

Linear discriminant analysis (LDA)

Similarly to PCA, linear discriminant analysis [15] (LDA) is a dimension-reducing method, in which we create background variables (called canonical variables, roots) by a linear combination of the variables of the original data matrix. LDA is a widely-used supervised pattern recognition technique. The main difference between PCA and LDA is that LDA is supervised, thus we need to know the class memberships of samples before the analysis. We can create $N-1$ canonical variables for N classes.

During LDA, we plot an ellipse (ellipsoid or a hyperellipsoid in the case of more than three variables) around each group of scattered points. The ellipse can be interpreted as a section plane of a Gaussian surface, which includes a given percentage of the points of the corresponding group. The center of the ellipse represents the maximum of the Gaussian surface. The discriminant function is given by the line connecting the intersections of the ellipses.

Classification and regression tree (CART)

CART [15,16] is a recursive classification method, which creates binary divisions from our dataset. The principle of

this method is to ask yes-or-no questions during the classification of the samples (i.e. the creation of a tree). The algorithm aims at identifying the possible variables and their values for the best resolution. The starting group is considered the root of the tree, which is always the group with the most samples. At the start, the other groups of samples are included in this group as well. Then the algorithm splits the samples to achieve the most advantageous separation of groups.

Its expressivity made it very popular in various field, such as data classification in medical diagnostics. Its theoretical basis was devised by Breiman, Friedman, Olshen and Stone in the 1980's [17].

Partial least-square regression discriminant analysis (PLS-DA)

PLS-DA is used for identifying outliers, ruling out variables with low variance (thus easing further studies) and mainly examining groupings of samples. [18-20]. PLS-DA is closely related to multivariate linear regression, to PCA, and to principal component regression. A possible implementation of the method is to apply matrix decomposition to the original \mathbf{X} and \mathbf{Y} data matrices, which are thus expressed as a product of three matrices. In case of (PLS-DA) the data matrix \mathbf{Y} contains the independent group variables.

Multivariate curve resolution with alternating least squares (MCR-ALS)

The method of multivariate curve resolution with alternating least squares (MCR-ALS) [21-23], as a chemometric method, can decompose the data matrix to profiles (composition profiles and pure elemental distribution profiles) with the use of certain constraints [24-26]. The usual assumption in multivariate resolution methods is that the experimental data follow a bilinear model similar to the Lambert-Beer law in absorption spectroscopy. In matrix form, this model can be described as

$$\mathbf{X}_{N \times M} = \mathbf{E}_{N \times L} \cdot \mathbf{C}_{L \times M}^T \quad (1)$$

where \mathbf{X} is the response matrix, \mathbf{E} is the elemental distribution profile matrix of the components, and \mathbf{C} is the composition profile matrix for the samples.

Suitably chosen initial estimations of \mathbf{E} or \mathbf{C} are optimized by solving Eq. (1) iteratively by alternating least squares optimization:

$$\begin{aligned} \mathbf{E}_{L \times N}^+ \cdot \mathbf{X}_{N \times M}^* &= \mathbf{C}_{L \times M}^T \\ \mathbf{X}_{N \times M}^* \cdot (\mathbf{C}_{L \times M}^T)^+ &= \mathbf{E}_{L \times N} \end{aligned} \quad (2)$$

where the matrix \mathbf{X}^* is the reproduced data matrix obtained by principal component analysis for the

selected number of components, and $^+$ means the pseudo-inverse of the original \mathbf{X} matrix [27]. Unfortunately, this decomposition is very often not unique because of the rotational and intensity (scaling) ambiguities [28,29]. The rotational ambiguities can be moderated or even eliminated if convenient constraints can be used [24-26]. Tauler and coworkers developed a Matlab code for MCR-ALS with some constraints [30].

Experimental

We have examined 289 silver coins provided by the Déry Museum of Debrecen. 32 coins were omitted from this dataset, because if only a small amount (3 or 4 pieces) was dated back to the time of a particular king, that set cannot be considered representative to that period. Four coins were identified with PCA as outliers in the early phase of research, so they were also omitted. Each measurement (spectrum acquisition and calculation of elemental composition) was carried out three times, with 30 seconds of irradiation. This time-span was found optimally short and precise by a prior investigation of several alloys. We have used the mean of the three measurements in cases, where elemental composition data were needed, and the three results separately, where X-ray spectra were needed. The amount of the following elements has been determined: Ti, Fe, Ni, Cu, Zn, Ag, Sn, Sb, Pb, Bi. The properties of coins were summarized in two tables: one containing the mean values of elemental composition (257×10), and the other containing intensity values for all studied wavelengths (257×2048). Two data matrices were created accordingly and evaluated by PCA, LDA, CART and PLS modules of the software STATISTICA 6.0; besides, MCR-ALS calculations were completed by PLS Toolbox V6.7.

Results and discussion

PCA results

First we pre-examined our variables. A correlation matrix (Additional file 1: Table S1) was created with the variables (metal concentrations) in its rows and its columns. Besides the correlation matrix, descriptive statistics were applied for the pre-examination. Both methods found all of the variables acceptable for further studies. The minima, maxima, standard deviations, medians and means of the variables were calculated in the pre-examination step (Additional file 2: Table S2).

Then, we carried out a PCA analysis on our standardized dataset and acquired the tables containing the scores (principal components) and the factor loadings. The number of scores was conveniently set to the number of variables, which in this case was not higher than ten. These ten principal components explained the total variance of the data, and 9 of them were linearly independent.

The scores were plotted in two ways. In the first case, the indicator variable had seven possible values, which represented three groups within the Árpád dynasty, three later dynasties and unknowns.

Figure 1 shows that some of the groups overlap heavily. The overlapped groups correspond to continuous time periods and they can be united. In the second figure the overlapped groups were united. Finally three groups were defined in total.

In both cases, the fifth score (an individual one) was plotted against the first score. Figure 2 shows that two large groups are separated well. The borderline is the beginning of the reign of king András II. This is coherent to numismatic facts, which suggest that certain ore treatment and coinage processes had undergone significant changes in this period. The correct classification rate was 75.8%. In every case the entire data set was used for classification, because theoretically that is the best possible classification.

Assignment of indicator variable values was:

I1 indicator variable: I2 indicator variable:

0: Unknown (18 coins) 0: Unknown

1: István I – Kálmán (997-1116) (30 coins) 2: István I – Imre:

2: István II – Imre (1116-1204) (60 coins) (997-1204) (90 coins)

3: András II – András III (1205-1301) (97 coins) 3: András II - Luxembourg

4: Czech (1301-1305) (5 coins) (1205-1437) (149 coins)

5: Anjou (1308-1387) (35 coins)

6: Luxembourg (1387-1437) (12 coins)

The same evaluation was carried out using spectral data instead of elemental compositions (Figure 3). We haven't used mean values, so three times more points were plotted as in the previous calculation. In this case the fifth score was plotted against the first one again.

LDA results

The same data matrix was used, but no spectral data were evaluated in this phase. I1 and I2 indicator variables were applied as grouping variables. Since LDA is a supervised method, grouping variables are necessary for the early classification of the samples to maximize the separation of the groups.

A calculation with the I1 indicator variable returned five concentrations as useful variables for classification, those are: iron, silver, bismuth, lead and tin. Based on maximizing the variance between the groups and minimizing it within the six groups in the classification matrix we could classify the 257 coins into three groups. By doing so, we have shown that the construction of the I2 indicator variable is valid.

In the case of the I2 grouping variable (two groups with the reign of András II as a borderline) iron, copper, bismuth, tin and nickel concentrations were identified by LDA as the best classifying variables.

Using the classification matrix for I2, we have created an I2b grouping variable, where the class membership for the misclassified 61 samples has changed, but the improved classification was not used further on.

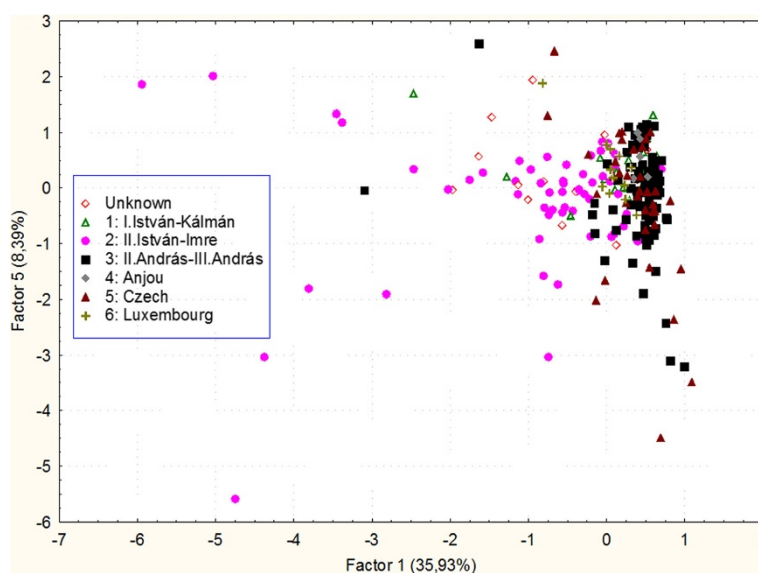


Figure 1 Most discriminating plots PC1 vs. PC5 (PC1 explains the largest portion of variance in the data) using original grouping.

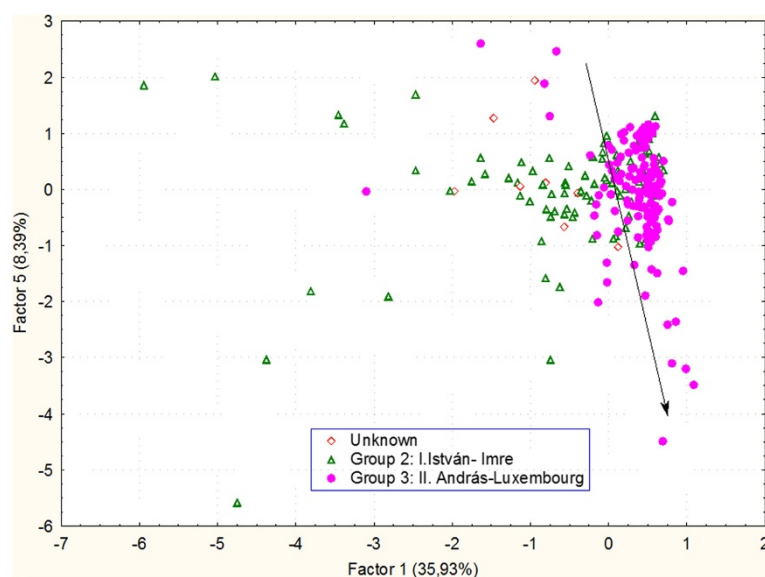


Figure 2 Most discriminating plots PC1 vs. PC5 after re-grouping of classes.

By performing LDA with our new grouping variable, we can observe a much better separation of the groups on Figure 4. The intersections of the ellipses (which contain 95% of their respective groups) can be intersected with a line. The correct classification rate was 76.6% for I2.

CART results

Two data matrices were used for *CART* analysis, the first one containing the unknown samples, the second one not. Applying the I2 grouping variable, the classification tree (Figure 5) contained four nodes based on four variables. First, all samples are included in the group with the most

samples, in this case, group 3. Unknown samples are separated based on the concentration of iron. Then, nodes were created based on the concentrations of copper, bismuth and zinc and the coins were separated from the periods before and after András II were separated. The decision tree can be interpreted with the following example: if the samples in the first node contain more than 1.05% iron than they are included in the group of unknowns, else in group 3. Then, group 3 is further classified into two groups based on the concentration of copper.

Classification was also carried out with unknowns omitted from the original dataset. With this calculation, we

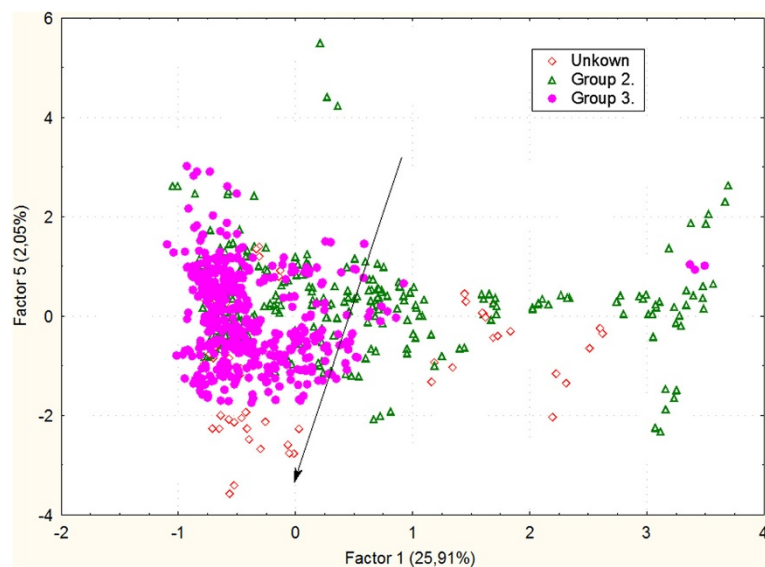


Figure 3 Plot of PC1 vs. PC5 from spectral data.

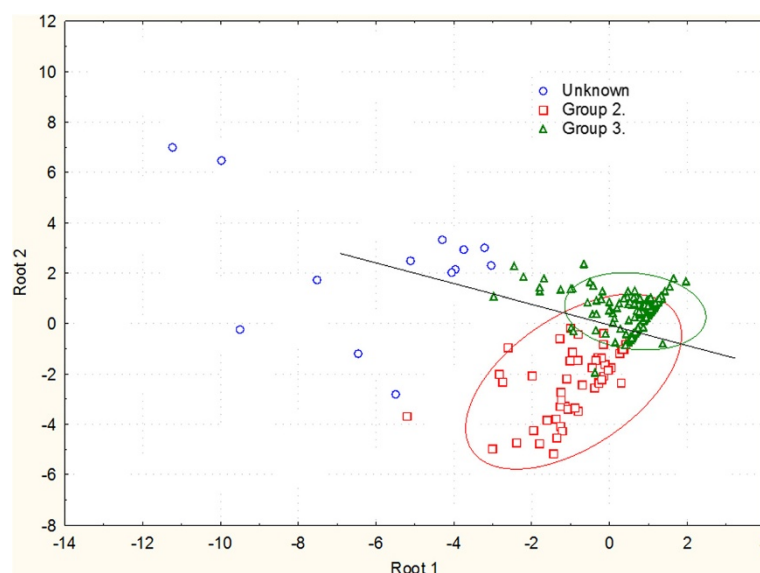


Figure 4 Plot of the most discriminating canonical variables (Root 1 against Root 2 canonical variables).

could test which groups would include the unknowns, if they didn't have a separate group in the first place. This analysis produced a decision tree (Figure 6) similar to the previous one. The correct classification rate was 78% (a threefold cross-validation provided a 3.4% uncertainty).

A more illustrative representation of the distribution of samples between the groups of the I2 and modified I2

(unknowns omitted) grouping variables is given by the following 3D histograms (Figure 7 and 8).

The analysis shows, that several samples from group 2 were included by CART in group 3 or into the unknowns. In the case of the modified I2 grouping variable, classification was more successful in terms of correct classification percentages.

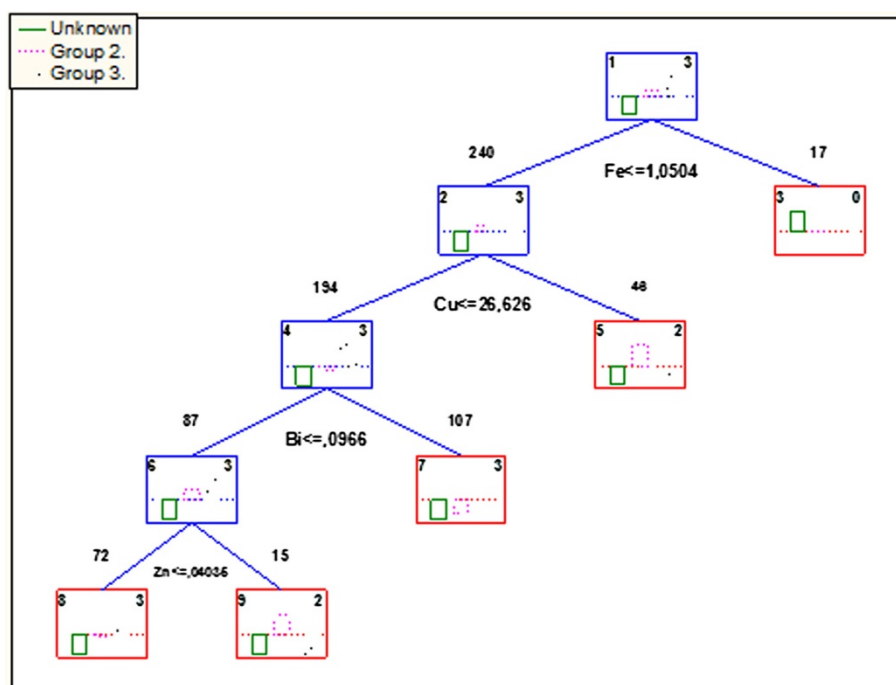


Figure 5 Classification tree for I2 with the unknown coins.

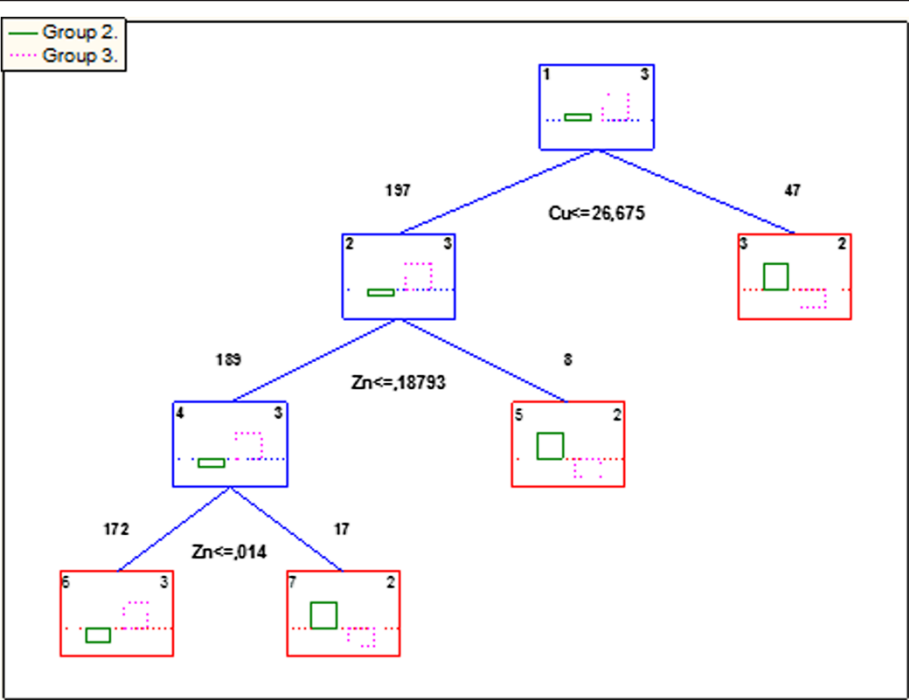


Figure 6 Classification tree for I2 without the unknown coins.

PLS-DA results

The samples were divided into two groups: a calibration group and a test group, with approx. 2:1 sample ratio. The number of latent variables (or PLS components) to be kept was determined with cross-validation. Plotting the PLS components (X-scores) against each other yields similar scatterplots as those produced by PCA. It should be noted

however, that unlike PCA, PLS is a supervised method, so the information, which is the basis of the classification of the coins is built into the model. The variable I2 yields the Y data matrix as a dependent variable. PLS components values for the X and Y data matrices are determined for each sample. For X, greater explained variance percentages and better classification were acquired; the final

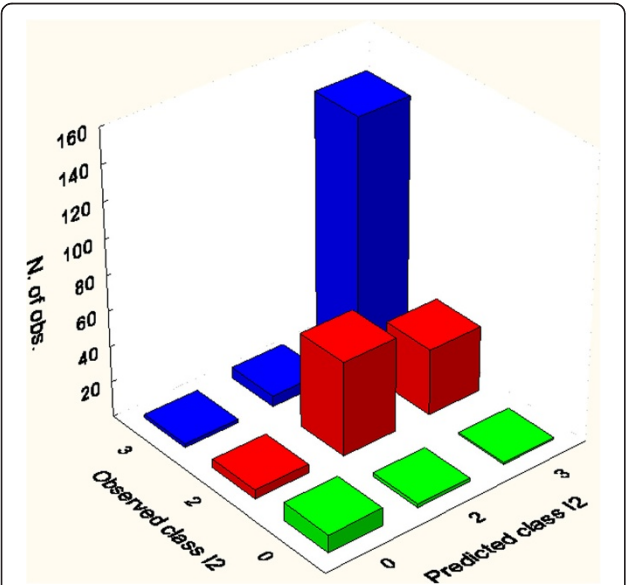


Figure 7 Correct classification percentages against grouping variables with unknown coins.

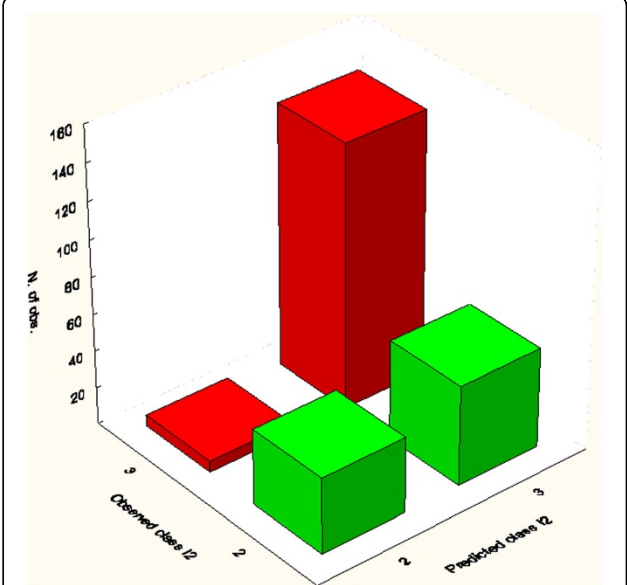


Figure 8 Correct classification percentages against grouping variables without the unknown coins.

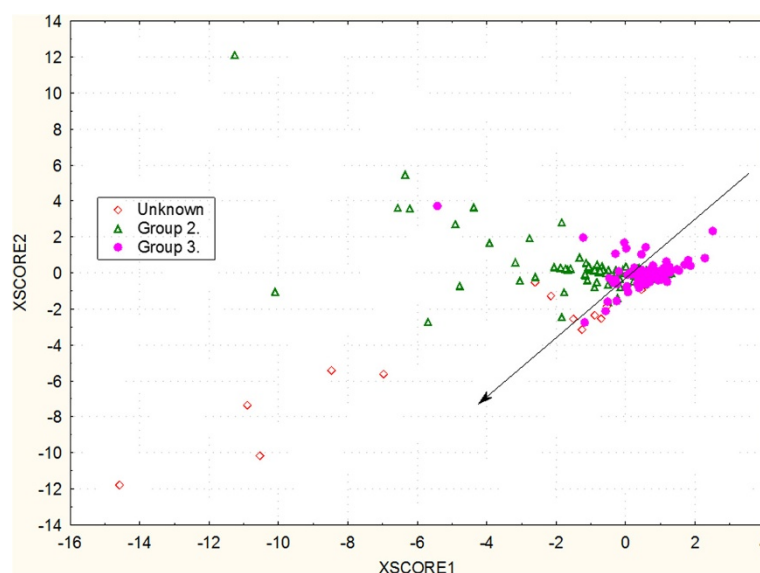


Figure 9 First and second components of X-scores against each other.

classification was carried out by plotting the first and second components of X against each other (Figure 9).

Although there is an overlap between the coins from before and after András II, (and there is a number of outliers among the coins from before András II), the two groups are separated to a satisfactory extent. The correct classification rate was 76.6%. The inclusion of unknowns is ambiguous in the cases of five coins, but the rest of the outliers can be included in one of the groups with sufficient probabilities.

MCR-ALS results

MCR-ALS can provide physically interpretable profiles, if proper constraints are used. The natural constraint is the non-negativity for both composition and distribution profiles. Figure 10 shows the elemental distribution profiles (MCR-ALS loadings). In the first latent variable (solid line), Cu, in the second (dash line), Pb, Cu and slightly Sn, in the third (dash-dot line), Sn, Cu, Zn and slightly Fe and Pb, and in the fourth (dot line), Ag dominate. Using the MCR-ALS scores for LDA we can classify the unknown coins. All unknown coins can be grouped into the first two groups based on I1 indicator variable. These coins highly probably belong to the Group 2 which is the union of the first two groups regarding I1 indicator variable.

Conclusions

With the introduction of several indicator variables, we can observe two well-defined groups in the PCA score plot. The clustering is justified by numismatic and historic theories, and supported by the results of other types of chemometric analysis. The precision of PCA evaluation is not increased by the use of X-ray spectra

instead of elemental compositions, because with the increasing amount of data, the amount of noise increases proportionally.

We have successfully classified the coins to their corresponding periods with a correct classification percentage of 76-78% based on X-ray fluorescence data with the use of four statistical analysis methods. This result is considered satisfactory, because the introduction of errors is not limited to the acquisition of spectra and the evaluation, but can also originate from the incorrect archaeological identification of the coins. If the group of unknowns was omitted, CART was the most successful method in classifying the samples to the correct groups. MCR-ALS based LDA could classify the unknown coins into the group 2 (István I-Imre).

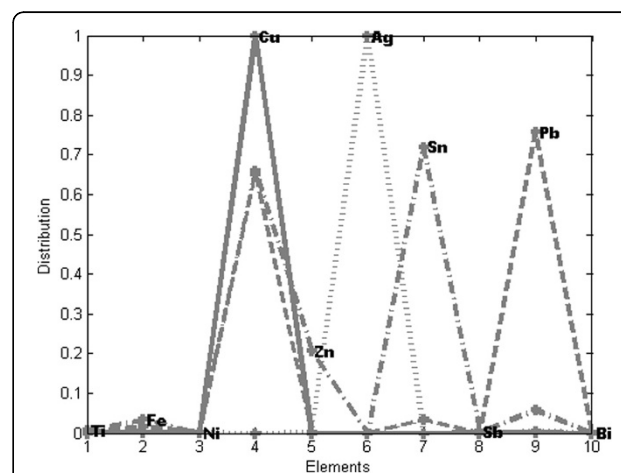


Figure 10 Elemental distribution of the four latent variables (components) calculated by MCR-ALS.

Elemental compositions of the silver coins from the Árpád Dynasty and the following dynasties were diverse, so overlaps between the groups are possible. Reasons for these overlaps range from counterfeiting to the bad condition of certain coins including the errors of archaeological identification.

However, determining the chemical composition of the coins and evaluating the data with chemometric methods can provide scientifically valid results to aid the archaeologists' and numismatists' work in classifying the coins according to their times of origin.

Additional files

Additional file 1: Table S1. Product moment correlation coefficients for measured metals in mediaeval coins.

Additional file 2: Table S2. Exploratory statistics for elemental composition of mediaeval coins.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

AR: Completed all X-ray measurements, participated in the statistical calculations (PCA, LDA, CART, PLS-DA) and wrote the manuscript draft, KH: participated in the statistical calculations (PCA, LDA, CART, PLS-DA). RR carried out the MCR-ALS calculations. JE: Formulated the aim and ensured the financial basis. All authors read and approved the final manuscript.

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